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On the Reaction Products of Lanthanide Chlorides with Biurete

T. A. Antonenko[a], *, L. Yu. Alikberova[a], D. V. Al'bov[b], V. V. Kravchenko[a], G. A. Fedorova[a], and N. S. Rukk[a]

[a] *Lomonosov State University of Fine Chemical Technologies, pr. Vernadskogo 86, Moscow, 117571 Russia*
[b] *Moscow State University, Leninskie gory, Moscow, 119992 Russia*
**e-mail: taisiya.antonenko@mail.ru*

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Abstract—The synthesis and results of IR spectroscopy and X-ray diffraction analysis of new complexes of biurete $NH_2CONHCONH_2$ (BU) with the composition $LnCl_3 \cdot 2BU \cdot 4H_2O$, where Ln = La (**I**), Pr (**II**), Ho (**III**), Er (**IV**), and Lu (**V**), are presented. Crystals of complexes **I–V** include complex cations $[Ln(H_2O)_4(BU)_2]^{3+}$ and uncoordinated chloride ions. The coordination mode of biurete molecules is bidentate through the oxygen atoms, and upon coordination the BU molecules are transformed from the initial *trans* to *cis* configuration. Water molecules are also coordinated through the oxygen atom (the shape of the polyhedron of the Ln atoms is a two-capped trigonal prism). The oxygen atoms of both BU molecules and the oxygen atoms of the first and second water molecules form a trigonal prism, whereas the oxygen atoms of the third and fourth water molecules form two caps of the coordination polyhedron. The coordinated BU molecules are joined with the chloride ions and water molecules of the adjacent complex cations by hydrogen bonds. The degree of conversion of *trans*-BU to *cis*-BU in the lanthanide series of complexes of this type is discussed.

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Biurete $NH_2CONHCONH_2$ (BU) is amide of allophanic acid (known only in the form of salts) and is formed as one of the thermal decomposition products of carbamide in the range from 150 to 170°C. Initially biurete was used in analytical purposes. Presently BU is used in a mixture with urea as a foaming agent in the production of sponge rubber, in particular, in special mixtures containing triboluminescence components with an additive of rare-earth metal salts [1], for the chemical activation of cellulose [2], and in other areas. An interesting feature of biurete is the presence of hydrogen bonds joining the adjacent molecules and, as a consequence, an affinity to form inclusion compounds, for example, nonstoichiometric hydrate $BU \cdot 0.8H_2O$ in the case of crystallization from aqueous solutions [3]. The structure of hydrate $BU \cdot 0.8H_2O$ includes tunnel cavities in which zigzag chains of the water molecules are localized.

A biurete molecule contains two carbonyl groups along with two amide groups and one imide group. Therefore, biurete can be coordinated by atoms of the complexing agent as a polydentate ligand. It is known that biurete has two tautomeric forms that can be coordinated as mono- or bidentate ligands [4]. The coordination through the oxygen atoms results in the transformation of biurete from the *trans* into *cis* form and the distortion of the planar BU molecule to this or another extent.

The study of the reactions of biurete with rare-earth metal salts has started more than fifty years ago, when the existence of the incongruently soluble compound $Ce(NO_3)_3 \cdot 2BU \cdot 5H_2O$ was first established [5]. Compounds $LnCl_3 \cdot 3BU \cdot 3H_2O$ (Ln = La, Ce, Pr, Nd, Sm, Gd, and Ho) were synthesized later [6]. In authors' opinion [6], in these compounds BU is coordinated by the bidentate mode through the oxygen atoms. However, the presence of water molecules introduces some uncertainty into the interpretation of the IR spectroscopic data.

Phase equilibria in $Pr_2(SO_4)_3$–BU–H_2O and $PrBr_3$–BU–H_2O systems were studied isothermally at 30°C [7]. The formation of crystalline complexes $Pr_2(SO_4)_3 \cdot 3BU$ and $PrBr_3 \cdot 3BU$ was established. The structures of the formed compounds were not studied. Phase equilibria in an ErI_3–BU–H_2O system were studied by the isothermal method at 25°C [8]. The formation of the incongruently soluble compound $[Er(BU)_4]I_3$ was established. It was proposed on the basis of the IR spectral data that in the obtained compound biurete is coordinated through the oxygen atom and manifests itself as a monodentate ligand.

The BU complexes with samarium nitrate and perchlorate $[Sm(BU)_4](NO_3)_3$ [9] and $[Sm(BU)_4](ClO_4)_3$ [10]; the biurete complexes of yttrium, gadolinium, and lanthanum chlorides [11–13]; and the BU complexes with scandium chloride and nitrate $[Sc(BU)(H_2O)_5]Cl_3 \cdot H_2O$ and $[Sc(BU)_4](NO_3)_3$ [14] were studied in detail. Complex cations $[Sm(BU)_4]^{3+}$ (the coordination number of Sm is 8, and the coordination polyhedron is a square anti-

Table 1. Elemental analysis results for complexes **I–V**

Complex	Content (found/calculated), %				Molar ratio $LnCl_3$: BU
	C	H	N	Ln	
$LaCl_3 \cdot 2BU \cdot 4H_2O$ (**I**)	9.22/9.24	2.95/1.93	15.72/16.17	25.50/26.54	1 : 2.04
$PrCl_3 \cdot 2BU \cdot 4H_2O$ (**II**)	9.05/9.14	3.00/1.90	15.71/15.99	26.92/26.82	1 : 1.97
$HoCl_3 \cdot 2BU \cdot 4H_2O$ (**III**)	9.08/8.74	3.07/1.82	15.72/15.29	30.02/30.02	1 : 2.06
$ErCl_3 \cdot 2BU \cdot 4H_2O$ (**IV**)	8.66/8.70	2.63/1.81	15.36/15.22	28.09/30.31	1 : 2.15
$LuCl_3 \cdot 2BU \cdot 4H_2O$ (**V**)	7.64/8.58	2.74/1.79	14.22/15.01	28.69/31.27	1 : 2.06

prism) and uncoordinated nitrate and perchlorate ions were observed in crystals of the BU complexes with samarium nitrate and perchlorate. The BU complex with scandium nitrate has a similar structure. The crystal structures of the BU compounds with yttrium and gadolinium chlorides contain complex cations $[Y(BU)_2(H_2O)_4]^{3+}$ or $[Gd(BU)_2(H_2O)_4]^{3+}$ (the coordination number of the rare-earth metal is 8, and the coordination polyhedron is a distorted square antiprism) and uncoordinated chloride ions [11, 12]. At the same time, the crystalline complex of lanthanide chloride with biurete contains single-charged complex cations $[La(BU)_2(H_2O)_2Cl_2]^+$ (the coordination number of La is 9, and the coordination polyhedron is irregular). The external sphere includes the chloride ion, two water molecules, and the oxonium cation [13]. Crystals of $[Sc(BU)(H_2O)_5]Cl_3 \cdot H_2O$ contain complex cations $[Sc(BU)(H_2O)_5]^{3+}$ (the coordination number of Sc is 7, and the coordination polyhedron is a distorted pentagonal bipyramid), uncoordinated chloride ions, and one out-of-sphere water molecule [14]. Hydrogen bonds that help the three-dimensional cross-linked structure to occur play an important role in all listed compounds.

The purpose of this work is the synthesis and structural study of the complexes of La, Pr, Ho, Er, and Lu chlorides with biurete.

EXPERIMENTAL

The starting compounds were biurete (high-purity grade) and lanthanum, praseodymium, holmium, erbium, and lutetium chloride hexahydrates obtained by the reaction of the corresponding oxides and carbonates with hydrochloric acid. The obtained solutions of lanthanide halides were evaporated on heating until crystals began to precipitate and cooled. The crystals were separated from the mother liquor by vacuum filtration on a porous glass filter and kept in a desiccator over sodium hydroxide to a constant weight.

Synthesis of complexes I–V was carried out at ambient temperature by mixing $LnCl_3 \cdot 6H_2O$ (Ln = La, Pr, Ho, Er, and Lu) and BU in a molar ratio of 1 : 2. For homogenation, several droplets of water were added to each reaction mixture until transparent solutions were formed. Hygroscopic prismatic light green (Pr), light orange (Ho), and light pink (Er) crystals, as well as colorless crystals (La, Lu), were isolated from the solutions after keeping in air.

Trilonometric titration was used for the determination of the lanthanide content in the obtained complexes [15]. The contents of C, H, and N were determined on a CHNS Flash EA1112 elemental analyzer (Thermo Finnigan, Italy). The determination error for C, H, and N was 0.2–0.3%. The compositions of the synthesized complexes correspond to the formulas given in Table 1.

IR spectra of biurete and complexes I–V were recorded on an EQUINOX 55 FTIR spectrometer (BRUKER, Germany) in the range from 400 to 4000 cm^{-1} (Nujol suspensions). The frequencies of the main absorption bands are listed in Table 2.

X-ray diffraction analysis of complexes I–V. Experimental intensities of diffraction reflections were obtained at ambient temperature (293(2) K) on a CAD-4 diffractometer (AgK_α radiation, graphite monochromator, ω scan mode). Unit cell parameters were determined and refined by 25 reflections in the θ ranges 12°–13° (**I**, **II**, and **V**), 13°–14° (**III**), and 11°–12° (**IV**). Selected experimental parameters and crystallographic characteristics of compounds **I–V** are given in Table 3. An absorption correction was applied by the ψ scan method for particular reflections. The primary processing of the experimental data array was performed using the WinGX program package [16, 17]. All subsequent calculations were performed in the framework of the SHELX-97 program package [18]. The crystal structures of the synthesized compounds were determined by direct methods followed by the refinement of positional and thermal parameters in the anisotropic approximation for all nonhydrogen atoms. Hydrogen atoms were introduced into the calculated positions and refined in the isotropic approximation by the riding model. The structures of complexes **I** and **II** are shown in Figs. 1–3, which were drawn using the MERCURY CSD 1.5 program [19]. The main geometric parameters of compounds **I–V** are listed in Table 4.

The coordinates of atoms and other parameters of the crystal structures of compounds **I–V** were deposited with the Cambridge Crystallographic Data Centre

Table 2. Frequencies of maxima of the main absorption bands (cm^{-1}) in the IR spectra of biurete and complexes **I–V**

Biurete		$[Ln(BU)_2(H_2O)_4]Cl_3$					Assignment of bands
[6]	This work	La	Pr	Ho	Er	Lu	
1325	1328	1332	1332	1331	1330	1330	δ(NH)
1420	1423						ν(CN) + δ(NH)
1500	1502	1480	1482	1489	1490	1491	ν(CN) + ν(C–NH_2)
1580	1588	1554	1556	1560	1561	1563	
1620	1625	1617	1618	1620	1605	1605	δ(NH_2)
		1640	1640	1631	1621	1623	
					1648	1649	
1680	1685	1682	1682	1678	1684	1684	ν(CO) + δ(NH_2)
1725	1725	1701	1700	1718	1708	1702	
3260	3253	3175	3180	3204	3190	3189	ν(OH) + ν(NH_2) + ν(NH)
3290	3414	3346	3347	3282	3347	3354	
3410				3367			

(no. 887957–887961; http://www.cc dc.cam.ac.uk, data_request@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The IR spectra of complexes **I–V** are of the same type. The transition of the biurete molecule from the *trans* to *cis* configuration upon the coordination by the lanthanide atom is interpreted [20] by the presence of strong absorption bands in the region corresponding to stretching vibrations of the C=O bond and an absorption band at 1500 cm^{-1}. The shift of absorption bands of stretching vibrations ν(CO) + δ(NH_2) to lower frequencies indicates that biurete is coordinated through the oxygen atoms. The splitting of the absorption band at 1620 cm^{-1} corresponding to bending vibrations δ(NH_2) into multiplets indicates possible distortions of the coordinated biurete molecule. The presence of broad diffuse absorption bands ν(NH) + ν(OH) at 3200–3400 cm^{-1} indicates the presence of coordinated water molecules.

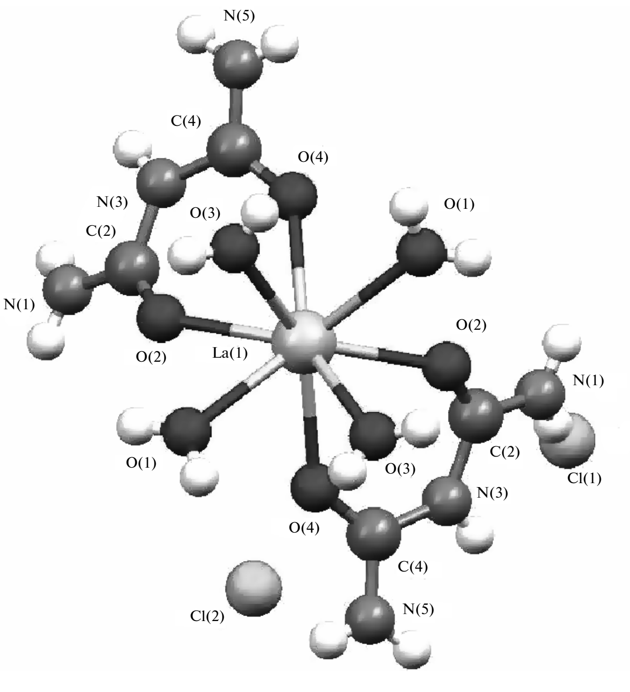

Fig. 1. Structure of compound **I**.

An X-ray diffraction analysis of isostructural crystals of complexes **I–V** of biurete with La, Pr, Ho Er, and Lu chloride hexahydrates showed that the crystals contained complex cations $[Ln(H_2O)_4(BU)_2]^{3+}$ (coordination number 8) and uncoordinated chloride ions (Fig. 1). The coordinated biurete molecules are

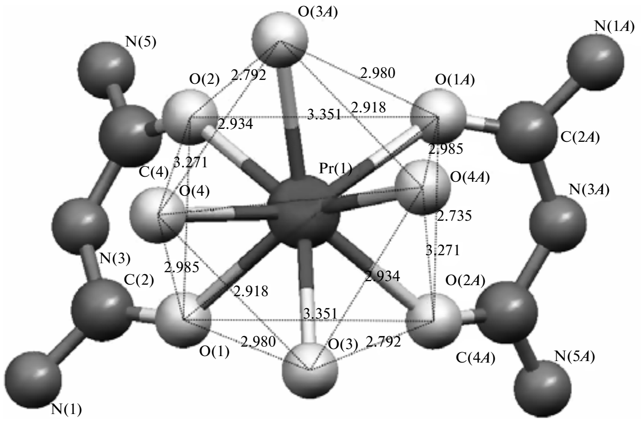

Fig. 2. Determination of the coordination polyhedron of the complex cation for compound **II** used as an example (hydrogen atoms of coordinated biurete and water molecules are omitted).

Table 3. Crystallographic characteristics and the experimental and refinement details for the structures of compounds **I–V**

Parameter	Value				
	I	**II**	**III**	**IV**	**V**
Empirical formula	$C_4H_{18}LaCl_3N_6O_8$	$C_4H_{18}PrCl_3N_6O_8$	$C_4H_{18}HoCl_3N_6O_8$	$C_4H_{18}ErCl_3N_6O_8$	$C_4H_{18}LuCl_3N_6O_8$
FW	523.50	525.50	549.51	551.85	559.55
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$
a, Å	7.741(2)	7.683(4)	7.610(4)	7.603(3)	7.607(3)
b, Å	12.830(3)	12.964(7)	13.169(6)	13.160(6)	13.158(5)
c, Å	17.983(7)	17.873(10)	17.254(8)	17.191(8)	17.137(8)
β, deg	101.55(4)	102.62(6)	100.66(4)	100.52(4)	100.53(4)
V, Å^3	1750.0(9)	1737.2(17)	1699.4(15)	1691.3(13)	1686.5(13)
T, K	293(2)	293(2)	293(2)	293(2)	293(2)
Z	4	4	4	4	4
ρ_{calcd}, g/cm^3	1.987	2.009	2.742	2.167	2.136
Radiation	AgK_α	AgK_α	AgK_α	AgK_α	AgK_α
μ(MoK_α), mm^{-1}	1.547	1.745	2.778	2.928	3.408
θ Range, deg	1.8–20	1.8–22	1.9–22	1.9–20	1.9–21
Range of indices	$-9 \le h \le 9$, $0 \le k \le 15$, $0 \le l \le 21$	$-10 \le h \le 10$, $0 \le k \le 17$, $0 \le l \le 23$	$-10 \le h \le 9$, $0 \le k \le 17$, $0 \le l \le 22$	$-9 \le h \le 9$, $-16 \le k \le 16$, $0 \le l \le 20$	$-9 \le h \le 9$, $0 \le k \le 16$, $0 \le l \le 21$
Crystal sizes, mm	0.2 × 0.2 × 0.2	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.3
Volume of experiment	1658	2156	2111	1610	1840
Independent reflections	1461	2016	1960	1443	1738
Number of refined parameters	137	117	137	137	137
Goodness-of-fit	0.923	1.162	1.121	1.063	1.050
R factor R_1/wR_2 ($I \ge 2\sigma(I)$)	0.0210/0.0287	0.0281/0.0304	0.0154/0.0192	0.0217/0.0279	0.0187/0.0208
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.311/–0.297	0.839/–1.345	0.460/–0.689	0.560/–0.826	0.703/–0.793

joined with the chloride ions and water molecules of the adjacent complex cations by hydrogen bonds, whose length is 3.17–3.25 Å (N–H···Cl), 2.88–2.97 Å (N–H···O), 3.16–3.23 Å (O–H···Cl).

The transformation of biurete into the *cis* form upon coordination by the lanthanide atom is caused by the rotation of the $-C(O)-NH_2$ fragment about the nitrogen atom of the imino group. As a result, the BU molecule becomes nonplanar, and the degree of coplanarity decreases monotonically in the series of lanthanides: the dihedral angles between the C(1)O(1)N(2) and N(2)C(2)O(3) planes in the coordinated biurete molecules are 27.03° (**I**), 25.36° (**II**), 21.75° (**III**), 21.50° (**IV**), and 21.67° (**V**). Probably, this decrease is observed due to the lanthanide contraction. The results obtained are consistent with the published data [10], according to which in the structure of compound $[Gd(BU)_2(H_2O)_4]Cl_3$ the dihedral angle between the C(1)O(1)N(2) and N(2)C(2)O(3) planes is 22.27°.

The aggregate test of the δ angles between the pairs of faces intersecting along edges of the b type [21] that bind four vertices of the B type to each other (the vertices in which five edges converge) was used to determine the shape of the coordination polyhedron of the rare-earth metal. Figure 2 shows that for the complex cation (using compound **II** as an example) the vertices of the B type are the O(4), O(4*A*), O(1), and O(1*A*) atoms. The O(1)O(2)O(2*A*)O(1*A*) = δ_1 = 7.11°, O(4)O(3)O(3*A*)O(4*A*) = δ_2 = 38.92°, O(4)O(3)O(2*A*)O(1*A*) = δ_3 = 31.61°, O(4*A*)O(3*A*)O(2)O(1) = δ_4 = 31.61°. Since in the trigonal prism $\delta_1 = 0°$, $\delta_2 = 21.7°$, and $\delta_3 = \delta_4 = 48.2°$, we used an additional criterion of the degree of "nonplanarity" of diagonal trapezoids [21]. For this purpose, we determined the φ angle between two planes: (1) the plane passing over the short base of the trapezoid and

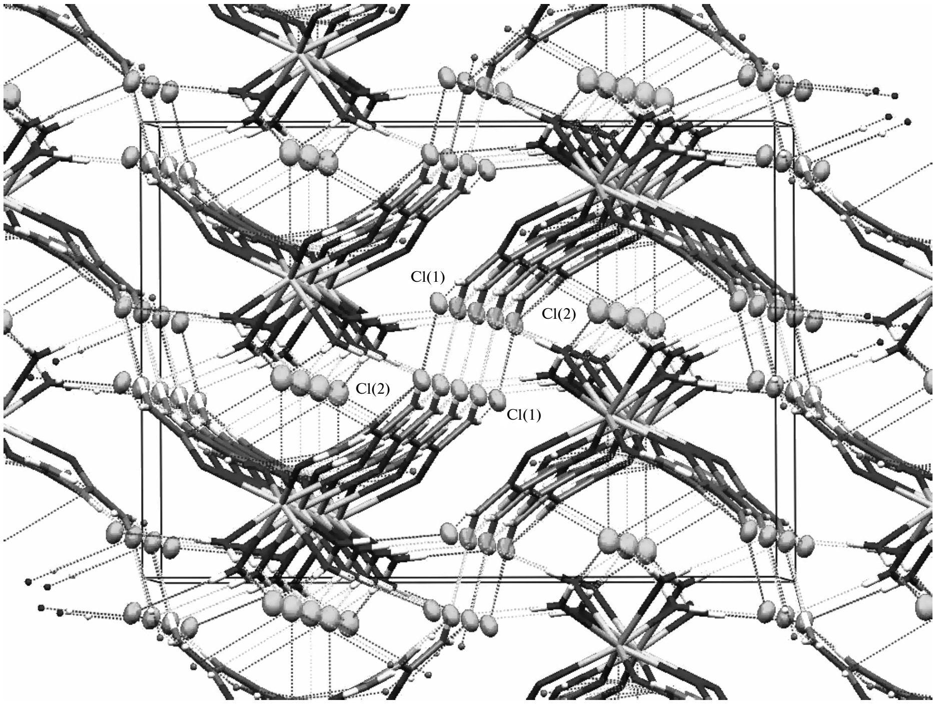

Fig. 3. Packing of complex **I**.

through the middle of the long base and (2) the plane passing over the long base of the trapezoid through the middle of the short base. The O(4)O(1*A*) and O(4*A*)O(1) edges serve as long bases of the trapezoid, while O(3)O(2*A*) and O(3*A*)O(2) are short bases (Fig. 2). The φ angles between the corresponding planes was 18.29°, whereas in an ideal two-capped trigonal prism φ = 16.1°, in an ideal dodecahedron it

Table 4. Selected bond lengths and bond angles in the structures of compounds **I**–**V**

Bond	*d*, Å				
	I	**II**	**III**	**IV**	**V**
Ln(1)–O(1)	2.535(2)	2.486(2)	2.361(2)	2.343(3)	2.313(3)
Ln(1)–O(2)	2.470(2)	2.428(2)	2.3314(17)	2.317(3)	2.302(2)
Ln(1)–O(3)	2.546(3)	2.487(3)	2.369(2)	2.359(3)	2.333(2)
Ln(1)–O(4)	2.448(2)	2.404(2)	2.3081(18)	2.291(3)	2.2858(19)
N(1)–C(2)	1.320(4)	1.320(4)	1.325(3)	1.318(5)	1.316(3)
C(2)–O(2)	1.225(3)	1.235(4)	1.237(3)	1.230(5)	1.230(3)
C(2)–N(3)	1.387(4)	1.380(4)	1.369(3)	1.380(5)	1.377(3)
N(3)–C(4)	1.377(3)	1.381(4)	1.375(3)	1.378(5)	1.380(3)
C(4)–O(4)	1.243(3)	1.241(4)	1.251(3)	1.240(5)	1.238(3)
C(4)–N(5)	1.308(4)	1.323(4)	1.304(3)	1.305(5)	1.331(4)
Angle	ω, deg				
N(1)C(2)N(3)	114.8(3)	115.5(3)	116.1(2)	115.1(4)	115.0(3)
C(4)N(3)C(2)	125.0(3)	124.7(3)	125.06(19)	124.3(3)	124.0(2)
O(4)C(4)N(5)	122.3(3)	122.1(3)	122.0(2)	122.2(3)	122.3(3)
O(4)C(4)N(3)	122.4(3)	122.4(3)	121.9(2)	122.7(4)	122.6(2)
N(5)C(4)N(3)	115.3(3)	114.7(3)	114.8(2)	114.1(4)	115.0(3)
C(2)O(2)Ln(1)	135.76(17)	136.37(18)	135.90(13)	135.9(2)	135.22(16)
C(4)O(4)Ln(1)	136.95(17)	136.80(18)	136.99(14)	136.8(2)	137.22(16)

is 0°, and that in an antiprism is 24.5° [21]. Therefore, it can be concluded that the shape of the rare-earth metal is a two-capped trigonal prism.

The packings of complexes **I–V** are of the same type. They include wave-like surfaces formed by the coordinated biurete molecules and uncoordinated chloride ions of the Cl(1) type (Fig. 3). The water molecules coordinated by the adjacent complex cation and chloride ions Cl(2) are localized in the cavities between the Cl(1) chloride ions. The system of N–H···O, N–H···Cl, and O–H···Cl hydrogen bonds stabilizes the packing and results in the three-dimensional cross-linked structures of the compounds.

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